

PELLET PROCESS FOR DOUBLE CURRENT COLLECTOR SCREEN
CATHODE PREPARATION

CROSS-REFERENCE TO RELATED APPLICATION

5

The present application claims priority on provisional application Serial No. 60/252,161, filed November 17, 2000.

10 BACKGROUND OF THE INVENTION

1. Field Of Invention

15 This invention relates to the conversion of chemical energy to electrical energy. In particular, the current invention relates to a new sandwich electrode design and a process for manufacturing the same. Sandwich electrodes are useful as the cathode in primary lithium cells and as the positive electrode in secondary lithium ion cells. These designs make such
20 cells particularly useful for powering implantable medical devices.

2. Prior Art

25 Early medical devices in many cases used at least two lithium electrochemical cells in series as their power source. However, the electronic circuits in these devices now consume less energy than before. This makes it currently possible to use a single lithium cell as a reliable power source. With a unitary cell design, the
30 requirement for high power density in many applications is even greater as the result of lowered pulsing voltage. Thus, a large electrode surface area is needed to accomplish this requirement. However, as the

electrode surface area increases, more inert materials (current collector, separator, etc.) are introduced into the system. As a result, the cell's volumetric capacity is decreased. Another concern is medical device
5 longevity, which is dependent on the cell's capacity and power efficiency.

An attempt to use high capacity materials, such as CF_x , by mixing it with a high rate cathode material, such as SVO, is reported in U.S. Patent No. 5,180,642 to
10 Weiss et. al. However, electrochemical cells made with these cathode composites have relatively lower rate capability. The benefit of increasing the cell theoretical capacity by using CF_x as part of the cathode mix is balanced, in part, by lowering its power
15 capability in a high rate discharge application, such as is encountered in an implantable cardiac defibrillator.

A significant solution to this problem is described in U.S. Patent Application Serial No. 09/560,060 entitled Sandwich Cathode Design For Alkali Metal
20 Electrochemical Cell With High Rate Capability by Gan et al., which is assigned to the assignee of the current invention and is incorporated herein by reference. This application describes a new sandwich electrode design using silver vanadium oxide (SVO) and a fluorinated
25 carbon (CF_x). An exemplary sandwich electrode has the following configuration:

SVO/current collector screen/ CF_x /current collector screen/SVO.

However, if the openings in the current collector
30 screen are too large, there can be communication of one of the active materials to the other side of the current collector during the manufacturing process. This

104645.0842

"contamination" is undesirable as it detracts from discharge performance. Specifically, SVO is of a higher rate capability, but a lower energy density than CF_x . Therefore, contamination of the interface between the current collector and one of the active materials by the other is undesirable as it defeats the purpose of having the respective active materials segregated on opposite sides of the current collector in the first place.

10 SUMMARY OF THE INVENTION

To maintain the improved discharge capability of a cell containing a sandwich electrode, it is necessary to maintain direct contact of both the first and second electrode materials with the opposed sides of the current collector. A good contact or adhesion translates into good interfacial conductivity during discharge. Although it is clear in theory, in practice this interfacial conductivity is highly influenced by the manufacturing methods or processes. When the current collector is a screen, it is possible for some of one of the electrode materials to pass through the current collector openings and become trapped between the other electrode material and the current collector. This leads to decreased interfacial conductivity between the current collector and the "contaminated" first electrode material.

Thus, the present process consists of having one of the electrode active materials in a cohesive form incapable of moving through the current collector to the other side thereof. However, in an un-cohesive form, the one electrode active material is capable of communication through the current collector. The other

or second active material is in a form incapable of communication through the current collector, whether it is in a powder form, or not. Then, the assembly of first active material/current collector/second active material is pressed from either the direction of the first electrode active material to the second electrode active material, or visa versa.

In that respect, the present invention is directed to an electrochemical cell, comprising: an anode; a cathode, wherein at least one of the anode and the cathode is characterized as having been formed by a method consisting essentially of: positioning a first electrode active material into a pressing fixture; positioning a first current collector screen on top of the first electrode active material; positioning a second electrode active material on top of the first current collector screen; positioning a second current collector screen on top of the second electrode active material; positioning a third electrode active material on top of the second current collection screen, thereby forming an electrode assembly; and pressing the electrode assembly to form the electrode; and a separator electrically insulating the anode from the cathode; and an electrolyte activating the anode and the cathode, wherein when the first and third electrode active materials are in an un-cohesive state, they are of an un-cohesive size less than an opening size of at least one opening of the current collector screen and capable of moving through the at least one opening, and wherein the first and third electrode active materials are in a cohesive form incapable of moving through the at least one opening in the current collector screen and

FOUO 434500

wherein the second electrode active material is in a form incapable of moving through the at least one opening in the current collector screen, and the electrode assembly is characterized as having been
5 pressed from the direction of either the first electrode active material to the third electrode active material or from the direction of the third electrode active material to the first electrode active material.

These and other objects of the present invention
10 will become increasingly more apparent to those skilled in the art by reference to the following description.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

15 The electrochemical cell of the present invention is of either a primary chemistry or a secondary, rechargeable chemistry. For both the primary and secondary types, the cell comprises an anode active metal selected from Groups IA, IIA and IIIB of the
20 Periodic Table of the Elements, including lithium, sodium, potassium, etc., and their alloys and intermetallic compounds including, for example, Li-Si, Li-Al, Li-B, Li-Mg and Li-Si-B alloys and intermetallic compounds. The preferred metal comprises lithium. An
25 alternate negative electrode comprises a lithium alloy, such as lithium-aluminum alloy. The greater the amount of aluminum present by weight in the alloy, however, the lower the energy density of the cell.

For a primary cell, the anode is a thin metal sheet
30 or foil of the lithium material, pressed or rolled on a metallic anode current collector, i.e., preferably comprising nickel, to form the negative electrode. In the exemplary cell of the present invention, the

04645.0842

negative electrode has an extended tab or lead of the same material as the current collector, i.e., preferably nickel, integrally formed therewith such as by welding and contacted by a weld to a cell case of conductive material in a case-negative electrical configuration. Alternatively, the negative electrode may be formed in some other geometry, such as a bobbin shape, cylinder or pellet to allow an alternate low surface cell design.

In secondary electrochemical systems, the anode or negative electrode comprises an anode material capable of intercalating and de-intercalating the anode active material, such as the preferred alkali metal lithium. A carbonaceous negative electrode comprising any of the various forms of carbon (e.g., coke, graphite, acetylene black, carbon black, glassy carbon, etc.) which are capable of reversibly retaining the lithium species, is preferred for the anode material. A "hairy carbon" material is particularly preferred due to its relatively high lithium-retention capacity. "Hairy carbon" is a material described in U.S. Patent No. 5,443,928 to Takeuchi et al., which is assigned to the assignee of the present invention and incorporated herein by reference. Graphite is another preferred material. Regardless of the form of the carbon, fibers of the carbonaceous material are particularly advantageous because they have excellent mechanical properties which permit them to be fabricated into rigid electrodes that are capable of withstanding degradation during repeated charge/discharge cycling. Moreover, the high surface area of carbon fibers allows for rapid charge/discharge rates.

A typical negative electrode for a secondary cell is fabricated by mixing about 90 to 97 weight percent "hairy carbon" or graphite with about 3 to 10 weight percent of a binder material, which is preferably a fluoro-resin powder such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyethylenetetrafluoroethylene (ETFE), polyamides, polyimides, and mixtures thereof. This negative electrode admixture is provided on a current collector such as of a nickel, stainless steel, or copper foil or screen by casting, pressing, rolling or otherwise contacting the admixture thereto.

In either the primary cell or the secondary cell, the reaction at the positive electrode involves conversion of ions which migrate from the negative electrode to the positive electrode into atomic or molecular forms. For a primary cell, the cathode active material comprises a carbonaceous chemistry or at least a first transition metal chalcogenide constituent which may be a metal, a metal oxide, or a mixed metal oxide comprising at least a first and a second metals or their oxides and possibly a third metal or metal oxide, or a mixture of a first and a second metals or their metal oxides incorporated in the matrix of a host metal oxide. The cathode active material may also comprise a metal sulfide.

Carbonaceous active materials are preferably prepared from carbon and fluorine, which includes graphitic and nongraphitic forms of carbon, such as coke, charcoal or activated carbon. Fluorinated carbon is represented by the formula $(CF_x)_n$ wherein x varies between about 0.1 to 1.9 and preferably between about

0.5 and 1.2, and $(C_2F)_n$ wherein n refers to the number of monomer units which can vary widely.

One preferred mixed metal oxide is a transition metal oxide having the general formula $SM_xV_2O_y$ where SM is a metal selected from Groups IB to VIIB and VIII of the Periodic Table of Elements, wherein x is about 0.30 to 2.0 and y is about 4.5 to 6.0 in the general formula. By way of illustration, and in no way intended to be limiting, one exemplary cathode active material comprises silver vanadium oxide having the general formula $Ag_xV_2O_y$ in any one of its many phases, i.e., β -phase silver vanadium oxide having in the general formula $x = 0.35$ and $y = 5.18$, γ -phase silver vanadium oxide having in the general formula $x = 0.80$ and $y = 5.40$ and ϵ -phase silver vanadium oxide having in the general formula $x = 1.0$ and $y = 5.5$, and combination and mixtures of phases thereof. For a more detailed description of such cathode active materials reference is made to U.S. Patent No. 4,310,609 to Liang et al., which is assigned to the assignee of the present invention and incorporated herein by reference.

Another preferred composite transition metal oxide cathode material includes V_2O_z wherein $z \leq 5$ combined with Ag_2O having silver in either the silver(II), silver(I) or silver(0) oxidation state and CuO with copper in either the copper(II), copper(I) or copper(0) oxidation state to provide the mixed metal oxide having the general formula $Cu_xAg_yV_2O_z$, (CSVO). Thus, the composite cathode active material may be described as a metal oxide-metal oxide-metal oxide, a metal-metal oxide-metal oxide, or a metal-metal-metal oxide and the range of material compositions found for $Cu_xAg_yV_2O_z$ is

preferably about $0.01 \leq z \leq 6.5$. Typical forms of CSV0 are $\text{Cu}_{0.16}\text{Ag}_{0.67}\text{V}_2\text{O}_z$ with z being about 5.5 and $\text{Cu}_{0.5}\text{Ag}_{0.5}\text{V}_2\text{O}_z$ with z being about 5.75. The oxygen content is designated by z since the exact stoichiometric

5 proportion of oxygen in CSV0 can vary depending on whether the cathode material is prepared in an oxidizing atmosphere such as air or oxygen, or in an inert atmosphere such as argon, nitrogen and helium. For a more detailed description of this cathode active
10 material reference is made to U.S. Patent Nos. 5,472,810 to Takeuchi et al. and 5,516,340 to Takeuchi et al., both of which are assigned to the assignee of the present invention and incorporated herein by reference.

In addition to the previously described fluorinated
15 carbon, silver vanadium oxide and copper silver vanadium oxide, Ag_2O , Ag_2O_2 , CuF_2 , Ag_2CrO_4 , MnO_2 , V_2O_5 , MnO_2 , TiS_2 , Cu_2S , FeS , FeS_2 , copper oxide, copper vanadium oxide, and mixtures thereof are contemplated as useful active materials.

20 In secondary cells, the positive electrode preferably comprises a lithiated material that is stable in air and readily handled. Examples of such air-stable lithiated cathode active materials include oxides, sulfides, selenides, and tellurides of such metals as
25 vanadium, titanium, chromium, copper, molybdenum, niobium, iron, nickel, cobalt and manganese. The more preferred oxides include LiNiO_2 , LiMn_2O_4 , LiCoO_2 , $\text{LiCo}_{0.92}\text{Sn}_{0.08}\text{O}_2$ and $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$.

To charge such secondary cells, lithium ions
30 comprising the positive electrode are intercalated into the carbonaceous negative electrode by applying an externally generated electrical potential to the cell.

FOETTY-FAST5007

The applied recharging electrical potential serves to draw lithium ions from the cathode active material, through the electrolyte and into the carbonaceous material of the negative electrode to saturate the carbon. The resulting Li_xC_6 negative electrode can have an x ranging between 0.1 and 1.0. The cell is then provided with an electrical potential and is discharged in a normal manner.

The above described cathode active materials, whether of a primary or a secondary chemistry, are formed into a sandwich electrode body for incorporation into an electrochemical cell by mixing one or more of them with a binder material. Suitable binders are powdered fluoro-polymers, more preferably powdered polytetrafluoroethylene or powdered polyvinylidene fluoride present at about 1 to about 5 weight percent of the cathode mixture. Further, up to about 10 weight percent of a conductive diluent is preferably added to the cathode mixture to improve conductivity. Suitable materials for this purpose include acetylene black, carbon black and/or graphite or a metallic powder such as powdered nickel, aluminum, titanium and stainless steel. The preferred cathode active mixture thus includes a powdered fluoro-polymer binder present at about 1 to 5 weight percent, a conductive diluent present at about 1 to 5 weight percent and about 90 to 98 weight percent of the cathode active material.

According to the present invention, two different ones of the above cathode active materials, whether of a primary or a secondary chemistry, are contacted to opposite sides of a current collector. Preferably, the first active material on the side of the current

collector facing the anode is of a lesser energy density, but of a greater rate capability than the second active material on the opposite side of the current collector and spaced from the anode. In other words, the exemplary second cathode active material never directly faces the lithium anode.

A preferred first cathode active material having a greater rate capability, but a lesser energy density is of a mixed metal oxide such as SVO or CSV0. This material is typically provided in a formulation of, by weight, about 94% SVO and/or CSV0, 3% binder and 3% conductive diluent as the formulation facing the anode. The second active material in contact with the other side of the current collector is, for example, CF_x. This material is preferably provided in a second active formulation having, by weight, about 91% CF_x, 5% binder and 4% conductive diluent.

Suitable current collectors are selected from the group consisting of stainless steel, titanium, tantalum, platinum, gold, aluminum, cobalt nickel alloys, highly alloyed ferritic stainless steel containing molybdenum and chromium, and nickel-, chromium- and molybdenum-containing alloys. The preferred current collector material is titanium, and most preferably the titanium cathode current collector has a thin layer of graphite/carbon material, iridium, iridium oxide or platinum applied thereto. Cathodes prepared as described above may be in the form of one or more plates operatively associated with at least one or more plates of anode material, or in the form of a strip wound with a corresponding strip of anode material in a structure similar to a "jellyroll".

Another exemplary cathode assembly has the following configuration:

When the openings in the current collector screen are of a greater size than the particle size of one of the active materials, it is possible for some of that active material to move through the openings and "contaminate" the contact interface between the current collector and the other active material. The specific nature of the contaminating material is not necessarily important in terms of whether it is the one having the greater energy density, but the lesser rate capability, or the other. The point is that any contamination of the active material/current collector interface by the other active material is undesirable.

According to one embodiment of the present invention, when one of the first and the second active materials is in an un-cohesive state and of a size less than that of at least one opening of the current collector screen, that material is capable of moving through the opening. An example of this is having the un-cohesive active material in a powdered form. Then, according to the present invention, this active material is rendered incapable of communication through the current collector by providing it in a cohesive state.

A cohesive state is defined as the active particles being held together firmly as part of the same mass, sticking together tightly, or having the particles of a body united throughout the mass. Examples of a cohesive state include providing the one active material being in a pressed pellet or in a sheet form.

A method of providing an active material in a sheet form is described in U.S. Patent Nos. 5,435,874 and 5,571,640, both to Takeuchi et al. and both assigned to the assignee of the present invention and incorporated herein by reference. These patents teach taking ground cathode active starting materials mixed with conductive diluents and a suitable binder material, and suspending the admixture in a solvent to form a paste. The admixture paste is fed into rollers to form briquettes or pellets, and then fed to rolling mills to produce the cathode active material in a sheet form. The sheet is finally dried and punched into blanks or plates of a desired shape.

Pellets are provided by pressing an active mixture under a pressure of about .1 ton/cm² to about 4 tons/cm², as is well known by those skilled in the art. Exemplary active materials and formulations which are readily capable of being pressed into a pellet form include, by weight, 91% SVO, 3% PTFE, 2% KETJENBLACK and 1% graphite; 91% CF_x, 4% PTFE and 5% Shawenigan Acetylene Black; 98% CF_x, 1% PTFE and 1% Shawenigan Acetylene Black; 100% SVO; 100% Ag₂O; and 100% AgO.

The other active material is comprised of particles that even when they are in an un-cohesive state, they are incapable of moving through the at least one opening in the current collector screen. In that respect, the

other active material is provided in the form of a pellet or a sheet or of a powder of particles sized too large to move through the current collector opening.

According to the present invention, the sandwich electrode is formed by pressing an assembly of the two active materials on opposite sides of an intermediate current collector from either a direction of the first cathode active material to the second active material, or visa versa. Since the one active material which could communicate through the current collector were it in an un-cohesive state is, in fact, in a cohesive form, and the other active material is incapable of communication through the current collector, whether or not it is in a cohesive form, the possibility of contaminating of either current collector/active material interface is eliminated.

Electrode structures of the present invention include the following:

first electrode active material/current collector screen/second active material/current collector screen/first electrode active material, wherein the first and second electrode active materials are different, or

first electrode active material/current collector screen/second electrode active material/second electrode active material/current collector screen/first electrode active material, wherein the first and second electrode active materials are different.

Another embodiment of the present invention has the following configuration:

first electrode active material/current collector screen/first electrode active material/second active

material/first electrode active material/current collector screen/first electrode active material, wherein the first and second electrode active materials are different.

5 In order to prevent internal short circuit conditions, the sandwich cathode is separated from the Group IA, IIA or IIIB anode by a suitable separator material. The separator is of electrically insulative material, and the separator material also is chemically
10 unreactive with the anode and cathode active materials and both chemically unreactive with and insoluble in the electrolyte. In addition, the separator material has a degree of porosity sufficient to allow flow there through of the electrolyte during the electrochemical
15 reaction of the cell. Illustrative separator materials include fabrics woven from fluoropolymeric fibers including polyvinylidene fluoride, polyethylenetetrafluoroethylene, and polyethylenechlorotrifluoroethylene used either alone or
20 laminated with a fluoropolymeric microporous film, non-woven glass, polypropylene, polyethylene, glass fiber materials, ceramics, polytetrafluoroethylene membrane commercially available under the designation ZITEX (Chemplast Inc.), polypropylene membrane commercially
25 available under the designation CELGARD (Celanese Plastic Company, Inc.) and a membrane commercially available under the designation DEXIGLAS (C.H. Dexter, Div., Dexter Corp.).

The electrochemical cell of the present invention
30 further includes a nonaqueous, ionically conductive electrolyte which serves as a medium for migration of ions between the anode and the cathode electrodes during

FOUO "SECRET"

10 A suitable electrolyte has an inorganic, ionically
conductive salt dissolved in a nonaqueous solvent, and
more preferably, the electrolyte includes an ionizable
alkali metal salt dissolved in a mixture of aprotic
organic solvents comprising a low viscosity solvent and
15 a high permittivity solvent. The inorganic, ionically
conductive salt serves as the vehicle for migration of
the anode ions to intercalate or react with the cathode
active material. Preferably, the ion forming alkali
metal salt is similar to the alkali metal comprising the
20 anode.

In the case of an anode comprising lithium, the alkali metal salt of the electrolyte is a lithium based salt. Known lithium salts that are useful as a vehicle for transport of alkali metal ions from the anode to the cathode include LiPF_6 , LiBF_4 , LiAsF_6 , LiSbF_6 , LiClO_4 , LiO_2 , LiAlCl_4 , LiGaCl_4 , $\text{LiC}(\text{SO}_2\text{CF}_3)_3$, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiSCN , LiO_3SCF_3 , $\text{LiC}_6\text{F}_5\text{SO}_3$, LiO_2CCF_3 , LiSO_6F , $\text{LiB}(\text{C}_6\text{H}_5)_4$ and LiCF_3SO_3 , and mixtures thereof.

Low viscosity solvents useful with the present
invention include esters, linear and cyclic ethers and
dialkyl carbonates such as tetrahydrofuran (THF), methyl
acetate (MA), diglyme, triglyme, tetraglyme, dimethyl

carbonate (DMC), 1,2-dimethoxyethane (DME),
1,2-diethoxyethane (DEE), 1-ethoxy,2-methoxyethane
(EME), ethyl methyl carbonate, methyl propyl carbonate,
ethyl propyl carbonate, diethyl carbonate, dipropyl
5 carbonate, and mixtures thereof, and high permittivity
solvents include cyclic carbonates, cyclic esters and
cyclic amides such as propylene carbonate (PC), ethylene
carbonate (EC), butylene carbonate, acetonitrile,
dimethyl sulfoxide, dimethyl, formamide, dimethyl
10 acetamide, γ -valerolactone, γ -butyrolactone (GBL),
N-methyl-pyrrolidinone (NMP), and mixtures thereof. In
the present primary cell, the preferred anode is lithium
metal and the preferred electrolyte is 0.8M to 1.5M
LiAsF₆ or LiPF₆ dissolved in a 50:50 mixture, by volume,
15 of propylene carbonate as the preferred high
permittivity solvent and 1,2-dimethoxyethane as the
preferred low viscosity solvent.

A preferred electrolyte for a secondary cell
according to the present invention comprises a solvent
20 mixture of EC:DMC:EMC:DEC. Most preferred volume
percent ranges for the various carbonate solvents
include EC in the range of about 20% to about 50%; DMC
in the range of about 12% to about 75%; EMC in the range
of about 5% to about 45%; and DEC in the range of about
25 3% to about 45%. In a preferred form of the present
invention, the electrolyte activating the cell is at
equilibrium with respect to the ratio of DMC:EMC:DEC.
This is important to maintain consistent and reliable
cycling characteristics. It is known that due to the
30 presence of low-potential (anode) materials in a charged
cell, an un-equilibrated mixture of DMC:DEC in the
presence of lithiated graphite (LiC₆~0.01 V vs Li/Li⁺)

Electrolytes containing the quaternary carbonate mixture
10 of the present invention exhibit freezing points below
-50°C, and lithium ion secondary cells activated with
such mixtures have very good cycling behavior at room
temperature as well as very good discharge and
charge/discharge cycling behavior at temperatures below
15 -40°C.

The cell header comprises a metallic disc-shaped body with a first hole to accommodate a glass-to-metal

seal/terminal pin feedthrough and a second hole for electrolyte filling. The glass used is of a corrosion resistant type having up to about 50% by weight silicon such as CABAL 12, TA 23, FUSITE 425 or FUSITE 435. The positive terminal pin feedthrough preferably comprises titanium although molybdenum, aluminum, nickel alloy, or stainless steel can also be used. The cell header is typically of a material similar to that of the case. The positive terminal pin supported in the glass-to-metal seal is, in turn, supported by the header, which is welded to the case containing the electrode stack. The cell is thereafter filled with the electrolyte solution described hereinabove and hermetically sealed such as by close-welding a stainless steel ball over the fill hole, but not limited thereto.

The above assembly describes a case-negative cell, which is the preferred construction of the exemplary secondary cell of the present invention. As is well known to those skilled in the art, the present secondary electrochemical systems can also be constructed in case-positive configuration.

It is appreciated that various modifications to the inventive concepts described herein may be apparent to those of ordinary skill in the art without departing from the spirit and scope of the present invention as defined by the appended claims.